(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
14 March 2002 (14.03.2002)

PCT

(10) International Publication Number
WO 02/20238 A1

(51) International Patent Classification[7]: B29C 44/10

(21) International Application Number: PCT/NL01/00653

(22) International Filing Date: 5 September 2001 (05.09.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data: 00203075.7 5 September 2000 (05.09.2000) EP

(71) Applicant *(for all designated States except US)*: ATO B.V. [NL/NL]; P.O. Box 17, NL-6700 AA Wageningen (NL).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: VAN TUIL, Robert, Frank [NL/NL]; Diedenweg 67-1, NL-6706 CJ Wageningen (NL). VAN HEEMST, Jacob, Johannes [NL/NL]; Jacob Catslaan 35, NL-4904 EK Oosterhout (NL).

(74) Agent: JORRITSMA, Ruurd; Nederlandsch Octrooibureau, Scheveningseweg 82, P.O. Box 29720, NL-2502 LS The Hague (NL).

(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 02/20238 A1

(54) Title: EXPANDED BIOPOLYMER-BASED ARTICLES AND PROCESS OF PRODUCING THESE

(57) Abstract: Three-dimensional foam mouldings made of a biodegradable thermoplastic polymer, in particular starch, and preferably a second biodegradable component can be manufactured in a discontinuous process by heating the polymer, in the form of an expandable bead or sheet or the like, in a mould having any desired shape under pressure in the presence of a blowing agent and subsequently depressurising. The second component can be used to enhance the water-resistance or the mould product and can be applied after, or preferably during or before the moulding step.

Expanded biopolymer-based articles and process of producing these

Introduction

[0001] The invention relates to three-dimensional foamed articles of a biopolymer. The biopolymer can be obtained from renewable raw materials, in particular starch. The articles can be used as disposables, packaging or filling material, and have the added functionality of being biodegradable. The invention also relates to the production of such foamed articles.

[0002] Foam materials for disposable packaging purposes have the reputation of damaging the environment. Recycling of such materials has not, as yet, taken off to any significant degree, because of the low density (and therefore high transportation cost) of these materials. The use of biodegradable foam materials in these applications is therefore a sensible alternative. Furthermore, the possibility to produce a packaging from fully renewable resources will help to reduce the consumption of raw materials.

[0003] A characteristic of many biopolymers, in particular those based on starch, is their sensitivity to water. This is a disadvantage for packaging material where contact with water/food can be expected. Thus, there is a need for foamed packaging and similar materials made of a water-resistant biopolymer or provided with a water-resistant biodegradable coating.

Prior art

[0004] WO92/02559 describes a method for extruding and injection-moulding thermoplastic starch. The mouldings thus obtained have a high density, i.e. more than 1000 kg/m^3, whereas 10-100 kg/m^3 is desirable for foam products for packaging, and in the case of thick-walled product entail high production costs (long cycle times).

[0005] EP 0 989 158 discloses a process for preparing foamed articles of biodegradable plastic material. This process consists of preparing foamed particles by expanding biodegradable plastic material, followed by submitting the particles to a heat treatment and/or to a treatment with a coating agent. Thus obtained particles are agglomerated to a foamed article by bringing the foamed particles into intimate contact with one another. A similar technique is disclosed in EP 0 594 977.

[0006] WO 99/57181 describes a mixture of materials that can be extruded to a water-resistant biodegradable foam. The extrudate can be used as loose-fill packaging material

or the extruded foam can be in the form of sheets which then can be thermoformed to desired articles.

[0007] US 6,030,673 (WO 96/05254) discloses a method for the preparation of moulded starch-bound containers and other articles. In this method a viscous mixture of a starch-based binder, filler material, a solvent and possible other additives is prepared. This mixture is fed into an article-forming apparatus where the solvent is removed from the mixture by applying heat and a cellular structure is formed. According to DE 4228779 (WO 94/05492), a composite shell material can be produced by foaming a 50% starch suspension of starch on a pre-shaped cardboard sheet; the foamed product is intended for packaging and has a density of 190 kg/m^3.

[0008] According to the methods known from the prior art, preparing foamed articles of biodegradable material involves complex mixtures of materials to achieve water resistance or complex and expensive article forming machinery requiring a large capital investment. Moreover, it is difficult, if at all possible, to produce articles with any desired three-dimensional shape using these known methods.

[0009] Therefore there is a need for a method that allows the production of water-resistant biopolymer-based foamed articles in any desired three-dimensional shape in an economically feasible way. The object of the present invention is to provide such articles and a method for their preparation.

Description of the invention.

[0010] A method has been found to manufacture truly three-dimensional biopolymer-based foamed articles. This method involves the manufacture in a rapid, discontinuous or semi-continuous process, of foamed articles by subjecting the biopolymer containing a blowing agent to an elevated temperature and pressure in a closed-off space, maintaining this situation for a certain period of time and followed by a rapid depressurisation causing the biopolymer to foam.

ing why
I after

[0011] The biopolymer is foamed within a mould having vent holes and the desired shape of the article, where the mould is enclosed in the closed-off space. The biopolymer can be provided with a water-resistant coating that either can be applied in the foaming process by foaming the biopolymer between water-resistant films or that can be applied afterwards.

[0012] The term biopolymer as used herein denotes three classes of polymers. Firstly, biopolymers include any polymer that can, as such, directly be extracted or otherwise

isolated from renewable natural resources. Examples thereof are polysaccharides and polypeptides. Post-modification of the polysaccharides or proteins by chemical and/or physical means is considered to be comprised in this class of biopolymers. Secondly, biopolymers include polymers that are obtained by non-natural (i.e. industrial) polymerisation of natural monomers or oligomers, i.e. monomers or oligomers produced from renewable resources. Examples thereof include poly(lactic acid). Thirdly, biopolymers as used herein include polymers obtained by biotechnological production, possibly but not necessarily including genetic modification of production organisms, from natural resources. Examples thereof comprise polyhydroxyalkanoates produced by suitable micro-organisms. In addition, other biodegradable, synthetic polymers can be used. Examples thereof include aliphatic polyesters and polyester-amides, polycaprolactone and the like.

[0013] The biopolymers to be used in the present invention should be melt-processable when they are subjected to the heat and pressure treatment for the purpose of forming foamed mouldings. The melt-processability can be inherent to the particular biopolymer, for example in the case of poly(lactic acid) or polyhydroxyalkanoic acids, or it can be achieved by subjecting the biopolymer to a particular treatment, such as mixing with plasticisers, thermomechanical treatment, heating and the like. Preferably, the melt-processable polymer is in a solid form, e.g. granules, powder or sheets, containing less than 30% of water on the basis of total weight of the polymer as introduced into the foaming mould.

[0014] Particularly suitable as a melt-processable biopolymer is thermoplastic starch. This starch is derived, for example, from potatoes, peas, wheat, rice, maize or tapioca, and is used as such or mixed with other biodegradable polymers such as cellulose (derivatives), other polysaccharides such as guar gum, locust bean flour, tragacanth, pectin, gum arabic or other gums, natural rubber, polyesters such as poly(caprolactone) and poly(lactic acid), proteins such a gluten and casein. Proteins and starch can also be added together in the form of flour. The other polymers can amount up to 75 wt.% of the mixture.

[0015] The thermoplastic starch can be based on native starch or alternatively on physically or chemically modified starch and special starches resulting from natural selection and/or genetic modification of starch-producing plants. Physically modified starch comprises inter alia starch modifications which are produced by ion exchange

(e.g. Na^+, K^+, Ca^{++}). Chemically modified starch and starch derivatives comprise oxidised, carboxymethylated, hydroxyalkylated starch and starch derivatised in some other way.

[0016] The starch is preferably admixed with a plasticiser such as a polyol (glycol, diethylene glycol or another glycol or polyalkylene glycol, glycerol, glycerol monoester, and the like), citric acid ester or a sugar polyol (for example sorbitol, lacticol) or (oligo)saccharide (for example glucose, sucrose, maltose and oligomers such as inulin and maltodextrins), or urea, but water on its own may also be sufficient. The amount of water can be, for example, 2.5-40 wt%, in particular 3-35 wt% based on the total amount of polymer. The amount of additional plasticiser such as glycerol is preferably 0-25 wt%, in particular 1-15 wt% based on the total amount of polymer. The polymer can further be admixed with an emulsifier such as lecithin or a monoglyceride, a release agent such as an oil (for example castor oil), a fatty acid or metal salt thereof (e.g. calcium stearate), a natural fibre such as flax or cellulose and/or a filler such as lime, chalk or nano-sized clay particles. Other possible additives are colorants, preservatives and in particular foaming agents as such sodium bicarbonate and nucleating agents such as talc. In addition, the composition can comprise mineral salts such as NaCl in an amount of, for example, 5-15% based on the total amount of biopolymer, which allow drastic modification of the foam structure.

[0017] Other biopolymers of the first class, such as cellulose, cellulose derivatives and proteins can similarly be transformed to a melt-processable polymer by addition of plasticisers and the like. Any of these biopolymers may be admixed with other, preferably (bio)degradable polymers such as polyvinyl acetate, polyvinyl alcohol, copolymers thereof with ethylene (EVOH), at a rate of up to e.g. 50%, preferably 0-30 % by weight of the other polymer.

[0018] The biopolymer is admixed with a blowing agent. Physical blowing agents such as low-boiling solvent and low-boiling plasticisers referred to above, in particular water or lower alcohols, or chemical blowing agents, e.g. azodicarboxylic esters or amides or benzenesulphonamide N-phenyl-hydrazide or a metal bicarbonate can be used as a blowing agent. Amounts can range from 1 to about 30% with respect to the total amount of biopolymer and plasticiser. The blowing agent can be added before or after the addition of further components such as plasticisers.

[0019] The polymer is shaped into a form which makes it suitable for the foaming process. This form can be referred to as an expandable bead or sheet or other shape. This can be done by thermomechanical treatment, in particular by extrusion, during which blowing agents and other additives can be present. Extrusion can result into granules or pellets in accordance with granulating or pelleting processes known per se, for example by extrusion in a twin-screw extruder at elevated temperature (60-200°C, for example for starch-based biopolymers in particular 100-150°C). The size of the granules is determined by the granulation rate and any grinding steps after granulation and the size can be that small that the granules can be referred to as powder. Instead of granules, sheets obtained by extrusion can be suitable forms for the subsequent foaming process. The sheets can be made from the biopolymers as such, with optional process aids, but they can also be coextruded sheets with a second component as described below.

[0020] The biopolymer granules/powder obtained can be conditioned to a moisture content that is optimal for the process. Depending on the basic biopolymer and on the content of other plasticisers, the moisture content after conditioning varies between 3 and 30%, for example for a starch-based biopolymer between 5 and 20% and for a cellulose diacetate-based polymer between 3 and 15%. Prior to the foaming step, the granules/powder can be coated in order to improve their mutual adhering capabilities.

[0021] The biopolymer granules/powder obtained are transferred to a mould, and foamed in the mould which has the shape of the desired article (referred to as product mould). The product mould is preferably enclosed in a larger closed-off space (referred to as foam mould). The mould cavity of the foam mould is connected to the outside environment through an outlet valve, being closed at the beginning of the process. The product can also be introduced into the foam mould by injection moulding. The foam mould is heated to the process temperature by continuous heating through injection of a flow of superheated steam or hot air or by continuous external heating or microwave heating of the foam mould until the internal temperature has attained the required temperature. In case of continuous heating, the superheated steam and/or hot air have a temperature, pressure and humidity adapted to the desired processing conditions in the foam mould. The processing conditions depend on the biopolymer being foamed and can range from 100 to 220°C and from 1 to 50 bar.

How i gen'c use htg

[0022] It can be beneficial to further increase the pressure in the mould. This can be done by applying an elevated initial pressure or by adding an additional amount of blowing agent in the mould. The pressure build-up prevents the boiling and subsequent evaporation of the blowing agent contained in the biopolymer. After a certain amount of time, the cavity of the foam mould is rapidly depressurised. This depressurisation causes an instantaneous gasification of the blowing agent followed by expansion of the biopolymer to a foamed article constrained by the physical boundaries of the product mould. The final article preferably has a density of 10-100 kg/m^3.

[0023] Advantageously, the foamed biopolymer is provided with a water-resistant coating, in case the biopolymer itself is not sufficiently water-resistant in view of the intended use of the moulded biopolymer. The water-resistant coating can consist of a second biodegradable component, which can be a biopolymer from one of the three classes of biopolymers as defined above. Such biopolymer can be made more water-resistant, if necessary, by derivatisation, such as esterification or etherification, e.g. in the case of starch or cellulose or another polysaccharide. In addition, other synthetic polymers or oligomers or waxes, preferably biodegradable, can be used as component for a water-resistant coating. Examples thereof include aliphatic polyesters and polyester-amides, polycaprolactone and the like. The final properties of the coating can be obtained by a final curing or cross-linking step.

[0024] There are several possible ways for applying the coating of the second component. Firstly, the coating can be applied during foaming (referred to as in-situ coating). In-situ coating can be done by separately introducing the second component into the product mould as a film or lining. When the biopolymer is foamed, the expanding foam will take the shape of the product mould, while simultaneously shaping the film and adhering to it. Secondly, this principle can be used by foaming a coextrudate of the biopolymer and the second component, e.g. in the form of a laminated sheet. In this way, adhesion between biopolymer and coating has been established before foaming. Thirdly, a coating can be applied by known means, e.g. dipping or spraying. This can be done with the biopolymer granules before foaming or with the foamed article after foaming. If required, a tie layer or adhesive layer can be used in to improve the adhesion of the coating to the polymer.

[0025] The process of the invention is a discontinuous or semi-continuous process. The mould to be used can have any desired shape, depending only on the shape of the

polymer articles to be produced. Therefore, the heating and pressurising/depressurising steps of the process are different from extrusion foaming processes which do not allow freedom of shape in the articles produced.

Example 1

[0026] Native potato starch, containing about 17 wt% of water, was made into melt-processable granules of about 3 mm diameter by extrusion under addition of water (about 20 wt%) and subsequent pelletisation of the extrudate. The extruded thermo-plastic starch granules were conditioned to a water content of 10-15 wt%. The conditioned granules were brought into a product mould and the filled product mould was placed in a foam mould and pressurised to 3 bar. A steam flow having a temperature of 190°C was used to heat the foam mould. The steam flow was maintained for 5 minutes, resulting in an internal temperature of the foam mould of 185°C. Simultaneously with discontinuing the steam flow, the foam mould was rapidly depressurised, causing the starch granules to expand to a foam. The resulting foam had a density of about 20 kg/m^3, consisted of closed cells, and had a homogeneously distributed cell size and shape with an average cell size ranging from 0.1 to 0.5 mm. Mechanical properties include a resiliency of 65%.

Steam ht which also 5min
ΔP

Claims

1. A process of producing a foam moulding made of a biopolymer, *characterised* in that the biopolymer is, or is transformed to a melt-processable polymer, and is heated in a mould having any desired three-dimensional shape under pressure in the presence of a blowing agent and subsequently is depressurised, said heating under pressure and depressurising being discontinuous.

2. A process according to Claim 1, wherein the biopolymer comprises starch, cellulose or a protein, or a derivative of starch, cellulose or a protein.

3. A process according to Claim 2, wherein the biopolymer is transformed to a melt-processable polymer by subjecting it to a thermomechanical treatment.

4. A process according to Claim 3, wherein the thermomechanical treatment is carried out in the presence of a plasticiser such as a polyol.

5. A process according to any one of Claims 1-4, wherein the biopolymer, prior to said heating under pressure, is brought in a form suitable for foaming by extrusion to granules or sheet.

6. A process according to any one of Claims 1-5, wherein the melt-processable biopolymer, prior to said heating under pressure, contains between less than 30 wt.%, preferably between 3 and 20 wt.% of water.

7. A process according to any one of Claims 1-6, wherein said heating under pressure is carried out at a temperature between 100 and 220°C and at a pressure between 1 and 50 bar.

8. A process according to any one of Claims 1-7, wherein a second component is coated onto the melt-processable polymer before or after said heating under pressure or before or after said depressurising.

9. A process according to Claim 8, wherein the second component comprises a starch derivative, a cellulose derivative, a polyester such as poly(lactic acid) or another poly(hydroxyalkanoic acid), or a copolyester such as a polyester amide.

10. A process according to Claim 8 or 9, wherein the second component and the biopolymer are co-extruded prior to said heating under pressure.

11. A process according to Claim 8 or 9, wherein the second component and the biopolymer are separately introduced into the mould and are simultaneously subjected to the heating under pressure.

12. A process according to Claim 8 or 9, wherein the second component is coated or laminated on the foamed moulding.

13. A moulding of a foamed biopolymer, obtainable by means of the process according to any one of the preceding claims.

INTERNATIONAL SEARCH REPORT

International Application No PCT/NL 01/00653

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B29C44/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B29C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 42 28 779 A (BIOTEC BIOLOG NATURVERPACK) 3 March 1994 (1994-03-03) cited in the application column 3, line 30 - line 56; claim 19	1-13
X	WO 96 05254 A (KHASHOGGI E IND) 22 February 1996 (1996-02-22) cited in the application page 21, line 15 -page 22, line 20; figure 1 page 61, line 18 - line 19 page 62, line 16	1-13

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
18 December 2001	27/12/2001

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Attalla, G

INTERNATIONAL SEARCH REPORT

International Application No PCT/NL 01/00653

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 018, no. 245 (M-1603), 11 May 1994 (1994-05-11) -& JP 06 032386 A (NISSEI KK), 8 February 1994 (1994-02-08) abstract -& DATABASE WPI Derwent Publications Ltd., London, GB; AN 1994-079841 XP002159088 abstract	1-13
A	WO 99 57181 A (UNIV NEBRASKA BOARD OF) 11 November 1999 (1999-11-11) cited in the application page 3, line 10 - line 11	4

INTERNATIONAL SEARCH REPORT

Int al Application No
PCT/NL 01/00653

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
DE 4228779	A	03-03-1994	DE	4228779 A1	03-03-1994
			AT	137165 T	15-05-1996
			CA	2143432 A1	17-03-1994
			CN	1083773 A ,B	16-03-1994
			DE	59302388 D1	30-05-1996
			DK	656830 T3	29-07-1996
			WO	9405492 A1	17-03-1994
			EP	0656830 A1	14-06-1995
			ES	2086961 T3	01-07-1996
			JP	8500547 T	23-01-1996
WO 9605254	A	22-02-1996	US	5660900 A	26-08-1997
			US	5783126 A	21-07-1998
			AU	705277 B2	20-05-1999
			AU	2971095 A	07-03-1996
			CA	2197059 A1	22-02-1996
			EP	0775173 A1	28-05-1997
			JP	10505369 T	26-05-1998
			NZ	289770 A	28-01-1999
			WO	9605254 A1	22-02-1996
			US	6030673 A	29-02-2000
			US	5662731 A	02-09-1997
			US	5705203 A	06-01-1998
			US	5843544 A	01-12-1998
			US	5776388 A	07-07-1998
			US	5868824 A	09-02-1999
			BR	9508540 A	19-05-1998
			US	5683772 A	04-11-1997
			US	5709827 A	20-01-1998
			US	5679145 A	21-10-1997
			US	5618341 A	08-04-1997
			US	5738921 A	14-04-1998
			US	5716675 A	10-02-1998
JP 06032386	A	08-02-1994	NONE		
WO 9957181	A	11-11-1999	US	6184261 B1	06-02-2001
			AU	3791199 A	23-11-1999
			WO	9957181 A1	11-11-1999